## PHILOSOPHICAL TRANSACTIONS.

I. On the Spectra of Ignited Gases and Vapours, with especial regard to the different Spectra of the same elementary gaseous substance. By Dr. J. Plücker, of Bonn, For. Memb. R.S., and Dr. J. W. Hittorf, of Münster.

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- 1. In order to obtain the spectra of all the elementary bodies, you may make use either of flame or the electric current. For this purpose flame is preferable on account of its easy management, and therefore was immediately introduced into the laboratory of the chemist. But its use is rather limited, the metals of alkalies being nearly the only substances which, if introduced into flame, give spectra exhibiting well-defined bright lines. In the case of the greater number of elementary substances the temperature of flame, even if alimented by oxygen instead of air, is too low. Either these substances are not reduced into vapour by means of flame, or, if reduced, the vapour does not reach the temperature necessary to render it luminous in such a degree that by prismatic analysis we obtain its characteristic rays. The electric current, the heating-power of which may be indefinitely increased by increasing its intensity, is alone fitted to produce the peculiar spectra of all elementary bodies.
- 2. In applying the electric current we may proceed in two ways. In one mode of proceeding the substance to be examined by its spectrum is at the same time, by means of the current, transformed into vapour and rendered luminous. In the other mode the substance is either in the gaseous state, or, if not, has been converted into it by means of a lamp, and the electric current ignites the substance in passing through.
- 3. The first way of proceeding is the least perfect, but we are obliged to recur to it in the case of all such elementary bodies as neither by themselves nor combined with other substances can be vaporized without altering the least-fusible glass. If the substance to be examined be a metal, the extremities of the conducting-wires are made of it and placed at a short distance from one another. When the strong spark of a large Leyden jar, charged by Ruhmkorff's powerful induction-coil, is sent through the space between the two extremities of the conducting-wires, minute particles of the metal,

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starting off from them, are volatilized: even in the gaseous state they conduct the electric current from point to point, and exhibit, while heated by it, the characteristic spectral lines of the metal. In all experiments made in this way, either air or another permanent gas occupied the space between the two extremities of the wires. The consequence of this is, the interposed gas partly conducting the electric current on its way through it, two spectra are obtained at the same time—the spectrum of the metal and the spectrum of the interposed gaseous medium. This inconvenience is the greater, as in most cases the number of bright lines constituting gas-spectra is a considerable one; it is least in the case of hydrogen, the spectrum of which, if appearing under these conditions, becomes nearly a continuous one (59). If the substance submitted to experiment be not a metal or charcoal, the extremities of the metallic wires are to be covered with it. Then we get with the spectrum of the non-conducting substance at the same time the spectrum of the metal covered by it.

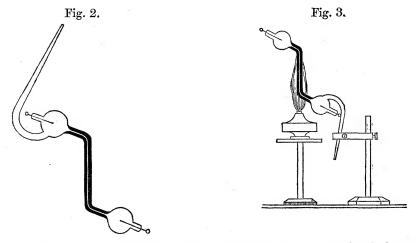
4. The spectra are obtained the most beautifully and are the most suitable for examination in their minute details, if the substance be in the gaseous state before the electric discharge is sent through it. The spectral tubes for enclosing gas, first proposed and employed by one of us, were in most cases, with some modifications, adopted for our more

Our tubes, as represented by the diagram (fig. 1), generecent researches. rally consist of a capillary middle part 30-40 millims. long, and 1.5-2 millims. in diameter, forming a narrow channel, by which two larger spheres, with platinum electrodes traversing the glass, communicate with one another. The small tube starting from one of the spheres serves to establish the communication with the exhauster, to which it is either attached by means of a cement (sealing-wax for instance), or soldered by the blowpipe. hauster, made solely of glass, without any metal, is connected with an additional system of glass tubes and glass cocks, by means of which the spectral tube is most easily filled with the gas to be examined. If the gas be a permanent one, the apparatus by which it is developed, and its accessory parts, by which it is purified and dried, may, as well as the spectral tube, simultaneously and separately be evacuated. The gas arrives directly from the apparatus into the tube, which, ad libitum, may be alternately filled and exhausted again. Finally, the tension of the gas is regulated and measured by means of a manometer in connexion with the exhauster.



- 5. In order to compare with one another the spectra corresponding to different densities of the gas, or even to a mixture of different gases, the tube may be examined by the spectroscope while attached to the exhauster. But generally the spectral tube was blown off and hermetically sealed at the extremity of the narrow tube starting from one of the spheres. This tube equally serves to attach the spectral tube before the slit of the spectroscope.
- 6. If the substance submitted to examination were at the ordinary temperature in the liquid or solid condition, the tube destined to receive it was made of a glass diffi-

cultly fusible, and bent as shown by the diagram (fig. 2). After having introduced into it a small quantity of the substance, the last traces of air were expelled from the tube, which was finally blown off. Put before the slit of the spectroscope, the enclosed substance was, by means of a lamp, reduced into vapour and, if necessary, kept in the gaseous state (fig. 3), and the density of the vapour regulated. The glass of our spectral tubes of this description is fused with such difficulty, that these highly evacuated tubes, when becoming red-hot by the lamp, are not altered by the pressure of the surrounding air.



- 7. Before giving a general account of the results we have obtained, it seems necessary to enter into some preliminary discussions regarding the admirable working of Geissler's exhauster, and the phenomena shown by our tubes when highly evacuated by it. essential part of Geissler's exhauster is a large glass ball, containing ten to twenty kilogrammes of mercury, which in its upper part communicates, by means of a doubly perforated stopcock of glass, either with the free air, or with the spectral tube to be From the lower part of the ball, which is invariably fixed, descends a longer tube of glass communicating at its lower extremity with a moveable similar tube, the free end of which enters into a large open bottle. When this bottle with the moveable tube is lifted up, the mercury within the apparatus entirely fills the ball, if commu-This communication having been interrupted, a Torricellian nicating with the air. vacuum is formed when the bottle descends. By establishing the communication with the spectral tube, the gas within it will be dilated. After the ascent and descent of mercury has thus been alternately produced often enough, no perceptible trace of air will remain within the spectral tube.
- 8. A tube evacuated in this way does not permit the induction current of Ruhmkorff's smaller apparatus (which in air gives a spark of about 15 millims.) to pass through. The current of his large apparatus forces a passage; but the spectrum we obtain in this case is very faint; it shows no traces of the bands of nitrogen, but solely the lines of hydrogen and the large fields of vaporized carbon (51). The hydrogen-lines take their origin from hygroscopic water covering the interior surface of the spectral tube, the carbon-bands probably from the minute traces of fatty matter hitherto employed in

greasing the stopcocks. (The oxygen simultaneously obtained by decomposition is not indicated.) The hydrogen-lines given by spectral tubes made of common glass are more brilliant than those of tubes made of less fusible glass, the hygroscopic state of the glass not being the same in both cases. Though within the interior of the exhauster the air is in contact with the surface of concentrated English sulphuric acid, or, what is preferable, with anhydrous phosphoric acid, we never succeeded in expelling the last traces of hygroscopic water, not even by strongly heating the spectral tube during evacuation.

If, in the usual way, a Leyden jar be intercalated into the current of Ruhmkorff's large induction coil, we must conclude, from the powerful charge of the jar, as proved by flashes of light, that within the spectral tube the tension of electricity, before it effects its passage, is very high. In this case the electric light is more bright, and of a fine colour like that of blue steel. When analyzed by the prism, it shows the spectral lines of hydrogen and oxygen, mixed with other spectral lines, among which those of sodium and silicium are the brightest. At the same time the interior surface of the capillary part of the tube tarnishes. Hence we conclude that the decomposed glass partly conducts the current.

By means of our tubes, therefore, the theoretical conclusions of Dr. FARADAY, that electricity being merely a peculiar condition of ponderable matter cannot exist without it, and cannot move without being carried by it, are confirmed and supported in a striking way\*.

- 9. As soon as the tube encloses perceptible traces of air, the spectral lines resulting from the ingredients of the glass entirely disappear. Though the temperature of the gas be raised by the passing current to an immense height, nevertheless, on account of its great tenuity and the short duration of the discharge, the gas is not able to heat the surface of the glass sufficiently to volatilize it. In this case also no spectral lines owing to particles starting from the platinum electrodes appear in the capillary part of the tube. Those lines are to be seen only near the electrodes, namely, in the aureola surrounding the negative pole.
- 10. The temperature of the particles of air seized by the weakest electric spark by far surpasses the temperature of the hottest obtainable flame. For no flame whatever shows the spectral lines of air, which are constantly seen in the spark. In order to raise the temperature of the discharge of Ruhmkorff's induction coil, you may either increase the power of the inducing current, or diminish the duration of the induced one. The last plan may be found preferable in most cases. The heat excited in a given conductor by a current sent through it increases in the ratio of the square of intensity, but decreases in the ratio of the duration of the current. Admitting, therefore, that the conductibility is not altered by elevation of temperature, and that the quantity of induced electricity remains the same, we conclude that the heating-power of the induced current is in the inverse ratio of its duration. But the resistance opposed by gases to the passage of

<sup>\*</sup> Mr. Gassior has already obtained vacua so nearly perfect as to present an obstacle to electric conduction. See Philosophical Transactions for 1859, p. 148.

electricity depends essentially upon their temperature. At the ordinary temperature it is rather too great to be measured, but, according to hitherto unknown laws, it rapidly decreases when the temperature rises beyond that of red heat. The law above mentioned is therefore not strictly applicable in the case of gaseous conduction.

11. Electricity can only be discharged through a given stratum of air, from one point to another, after a certain electric tension takes place in these points. This tension depends upon the chemical constitution of the gas, and, the gas being the same, it is nearly in the ratio of its density and the distance of the two points. The quantity of electricity required to produce that degree of tension which must precede the electric discharge through our spectral tubes, enclosing gas of a given density, may be indefinitely increased by interposing a Leyden jar. The less the distance between the coatings of the jar, and the larger their surface, the greater quantities of electricity will be accumulated on them, ready for discharge at the moment when the electric tension of the electrodes entering our tube reaches that intensity which alone allows the discharge to take place. Thus the Leyden jar is the most proper and most easy means for shortening the duration of the discharge, and consequently increasing the temperature of the gas.

In several cases, especially if a vapour like that of mercury be examined, which isolates less, it will be found more convenient, instead of replacing the Leyden jar by a larger one, to increase the charge of the same jar by intercalating into the circuit a spark micrometer, by means of which you may add to the resistance within the spectral tube the resistance of any stratum of air.

- 12. The leading idea by which one of us was guided when he first (1857) directed his attention to spectral analysis, was to concentrate the light in Geissler's tubes by confining the electric current within a capillary channel\*. The construction of our tubes immediately follows from it. Accordingly we gave, for different purposes, a different diameter to their capillary part. The length of this part is of very little influence if the tubes are very highly exhausted; we had to shorten our recent tubes, intended to enclose gases and vapours of a greater density, rendered luminous by a powerful induction coil.
- 13. We employed in our researches the large spectral apparatus constructed by M. Steinheil. The refracting angle of one of the four flint prisms belonging to the apparatus is 60°, the angle of the three others 45°. Generally we made use of only two prisms (of 60° and 45°), and of a magnifying power of only 18.

It is well known that the slit of the apparatus, if illuminated by sodium-light (by the flame of alcohol containing common salt), is seen double. According to the width of the slit and the dispersive power of the prisms, the two well-defined images, having both

\* PLÜCKER: "Spectra der elektrischen Lichtströmungen," 30 März 1858, Poggendorff's 'Annalen,' vol. civ.; "Ueber die Spectra der verschiedenen Gase, wenn durch dieselben bei starker Verdünnung die elektrische Entladung hindurchgeht," 25 Aug. 1858, Ibid. vol. cv.; "Ueber die Constitution der elektrischen Spectra von verschiedenen Gasen und Dämpfen," 5 Mai 1859, Ibid. vol. cvii.

the breadth of the slit as observed without the interposed prisms, are either superposed, or touch one another, or are separated by a black space. In making use of the two prisms, we generally regulated the aperture of the slit so that the two small sodiumbands appeared separated by a black space having nearly the breadth of these bands. In this case the angle at which the aperture of the slit is seen is equal to half the angular distance of the two middle lines of the bands, and therefore equal to half the angular distance of the two sodium-bands themselves after being reduced by narrowing the slit to mathematical lines.

If the images touch each other, the aperture of the slit and the two sodium-lines are seen at the same angle.

14. The first fact which we discovered in operating with our tubes, guided by the above explained principles, was the following one:—

There is a certain number of elementary substances, which, when differently heated, furnish two kinds of spectra of quite a different character, not having any line or any band in common.

The fact is important, as well with regard to theoretical conceptions as to practical applications—the more so as the passage from one kind of spectra to the other is by no means a continuous one, but takes place abruptly. By regulating the temperature you may repeat the two spectra in any succession ad libitum.

We will now treat more explicitly the case of *Nitrogen*, which first unfolded to us its different spectra. These spectra, obtained in the easiest and most striking way, have been examined by us in every point of view. The other cases of double spectra may hereafter be spoken of in a more summary manner.

- 15. We examined nitrogen prepared in different ways, even in the state of greatest purity; but we found that, in order to get pure spectra of it, it was not necessary to free the gas from all traces of air \*. Therefore we may select the following preparation, imperfect as it is, in order to give an instance of constructing nitrogen-tubes. Three absorbing apparatus were connected with one another and, by means of a stop-cock, with the exhauster, the first two being filled with a solution of pyrogallic acid in hydrate of potash, and the third with concentrated sulphuric acid. After having evacuated the interior of the exhauster and the spectral tube connected with it, by carefully turning the stopcock air was very slowly admitted, leaving its oxygen and carbonic acid to the first two, and its aqueous vapour to the third absorbing apparatus. Thus by and by the exhauster, with the tube, was filled with nitrogen, the manometer always indicating the tension of the gas. These operations being repeated several times by alternately evacuating and introducing new nitrogen, finally, the tension of the gas
- \* Whatever may be, under certain conditions, the practical importance of prismatic analysis in detecting certain substances converted into vapour, whatever may be its use in indicating traces of a single gas imperceptible by other means, mixtures of permanent gases are not fitted to be examined by the prism. A gas, if mixed in rather small proportion with another one, entirely escapes observation. The proportion necessary to render it visible depends upon the nature of the gas as well as upon the temperature of ignition.

(measured by means of the manometer) being from 40 millims. to 80 millims., the spectral tube was melted off and hermetically sealed.

- 16. When we send through our nitrogen-tube the direct discharge of RUHMKORFF'S large induction coil, without making use of the Leyden jar, we observe a beautiful richly coloured spectrum. This spectrum is not a continuous one, but divided into bands, the character of which differs essentially at its two extremities; its middle part Towards the more refracted part of the spectrum, is in most cases less distinctly traced. the bands, illuminated by the purest blue or violet light, present a channeled appearance\*. This effect is produced by a shading, the intensity of which decreases from the more to the less refracted part of each band. On applying four prisms instead of two, we perceive a small bright line, forming an interstice between two neighbouring channels, and the shading is, by the telescope of the spectral apparatus, resolved into dark lines. The number of such dark lines of one of the brightest bands (of the eighth band, we always count from the red to the violet) was found to be thirty-four, or nearly so. Their mutual distance is nearly the same, but their darkness decreases towards the leastrefracted limit of each channeled band. Hence we concluded, the breadth of the band having been measured, that the angular distance of two contiguous shading-lines was nearly equal to the distance of the two sodium-lines. The breadth of the channeled bands varies, but the character of all is absolutely the same; only if foreign bright lines like those of hydrogen are simultaneously seen, it becomes slightly disturbed. We may distinguish seventeen bands of this description; the first three are smaller ones, the fourth is traversed by H $\beta$ , the eleventh by H $\gamma$ †. At the violet extremity the light is very faint.
- 17. The bands of the less refracted part of the spectrum are all of nearly the same breadth, but smaller than those just described, and of quite a different appearance. Making use of only a single prism, and of a small magnifying power, we count eighteen such bands, starting from the extreme red and extending to the greenish yellow, where they are bounded by a dark space. Ha falls within the fourth, and the double sodium-line (Na) within the fourteenth of these bands. Under favourable circumstances, both extremities of the spectrum being equally developed, these bands extend to the channeled part, their number rising to thirty-five. All have the same general character, but not the same brightness. From the extreme red the intensity of light
- \* Under favourable conditions such a band appears furrowed semicircularly; but psychological effects of this description may be quite different: partly by our own will, partly by exterior circumstances, the bands may be seen convex as well as concave. Even the engraving of the bands (Plate I.) shows it. Let it be illuminated by daylight through a window, you will see the bands concave if their more refracted and shaded part be directed towards the window; if in the opposite direction, the bands will appear convex. The shade passes from one side to the other if really concave and convex bands are replaced by one another; so it does if the illuminating light pass to the opposite side. Accordingly, the stereoscopic appearance depending upon the direction from which the light comes, the mind passes judgment on it unconsciously.
- † We denote by  $\text{H}\alpha$ ,  $\text{H}\beta$ , and  $\text{H}\gamma$  the three bright lines of the spectrum of hydrogen (the red, the bluish green, and the violet one). See 57.

increases to the eighth band; over the ninth, tenth, and eleventh, especially over the two last, a shadow is spread, which gives to the red a rather brownish tint. The next seven bands are of a fine orange and yellow colour. The nineteenth and twentieth bands are very dark, the twenty-first is less dark. The following bands have a green colour, varying in brightness. The darkest are the twenty-eighth and twenty-ninth, succeeding the lightest ones.

The cause producing these bands and their shading by dark transverse lines is evidently not the same as that which produces the shadow overspreading some of them. This may be concluded, for instance, from the fact that the shadow which darkens the nineteenth and twentieth bands, without entirely destroying their limits, spreads at the same time over the neighbouring third part of the preceding eighteenth band.

18. When the light sent out from the incandescent nitrogen within the capillary tube is dispersed by means of four prisms, the shading of the less refracted bands also is resolved into dark narrow lines; but these lines are smaller than the similar lines of the more refracted bands, and their distribution quite different. If the dispersion increase, in each band we at first perceive a new dark limit; but the design becoming gradually more defined, we observe in each band extremely delicate bright lines bounded by a shadow or by dark lines.

By closer examination of a band we distinguish first a least-refracted small part, occupying about the seventh part of the whole, formed by two bright lines including a somewhat larger dark space. The first of these two bright lines touches the dark extremity of the preceding band; the second is bounded by a subtle dark line, to which succeeds a third bright line, smaller than the two first. A fourth bright line divides the whole band into two parts, one less refracted, comprising the small one just described, the other more refracted and larger—the breadth of the two parts being about in the ratio of 4:5. Starting from the bright middle line, a feeble shading is produced by a number of most subtle dark lines, the darkness of which decreases towards the least-refracted part. Similar but darker lines produce the stronger shading of the larger more refracted part, decreasing in the same direction from the extremity of the whole band towards its bright middle line. The stereoscopic effect produced by the shading of the bands is represented by the diagram (Plate I.).

The configuration of all the bright orange and yellow bands is exactly the same; it is rather obscured in the case of the preceding bands by the shadow spreading over them, but becomes the same again in the bright red ones. Even in the dark bands 19 to 21, traces of the design are to be seen. The appearance of the green bands, though the general character be the same, slightly differs; the shading in the middle part of them being increased, they rather seem to be divided into two.

The accordance of these bands, even to the minute detail of their configuration, is a fact worthy of attention.

19. The character of the two systems of bands on the extremities of the spectrum is

entirely stereotype; all apparent changes result from the different intensity of light. The middle part of the spectrum, on the contrary, may much differ from that which we have described; you may even say that this part varies more or less essentially on replacing one spectral tube enclosing nitrogen by any other. Sometimes the traces of the less refracted bands are seen far beyond  $H\beta$ , spreading over the channeled part of the spectrum; in other cases the channeled appearance goes in the opposite direction as far as the sodium-line, disturbing the character of the bands.

- 20. Now, instead of the direct discharge of Ruhmkorff's large induction coil, let us send through the very same spectral tubes the discharge of the interposed Leyden jar. The spectrum then obtained (Plate II.) has not the least resemblance to the former one. The variously shaded bands which we have hitherto described are replaced by brilliant lines on a more or less dark ground. Neither the distribution of these new lines nor their relative brightness gives any indication whatever of a law. Nevertheless the place occupied by each of them remains under all circumstances invariably the same. If exactly determined, not only does each line undoubtedly announce the gas within the tube, but the gas may even, without measuring, be recognized at first sight by characteristic groups into which the lines are collected.
- 21. The new spectrum of nitrogen extends towards the red slightly beyond the hydrogen-line  $H\alpha$ , which if the gas be not dried with care will be seen simultaneously, enclosed by two red nitrogen-lines, the less refracted of which is twice as distant as the more refracted. There are in the spectrum five groups of brilliant lines especially The orange group, slightly less refracted than Na, is formed by four lines, the second of which is the brightest; the third, not quite so bright, is closely followed by the fourth, which is very faint. The second (yellow) group contains seven lines, among which the fifth is brightest. The third (light-green) and the fourth (dark-green) group contain each nine lines. The third and sixth lines of the light-green group and the sixth and seventh (both near to each other) of the dark-green group are brightest. The fifth (light-blue) group (the distance of its middle part from H $\beta$  and H $\gamma$  is about in the ratio of 3:4) is formed by six lines, the second of which is the brightest, the first slightly less bright; the last four lines, nearly equally distant from each other, are slightly less bright again. Two groups, of three fainter lines each, fall between the two green groups and between the dark-green and the blue. We may mention also two bright single lines, placed out of the groups—a green line preceded by an expanded one, and a light-violet line followed at a short distance by a bright band. there are in the spectrum more or less faint bands or expanded lines extending beyond Hy nearly as far as the distance between this line and H $\beta$ , i. e. about to Fraunhofer's line H.
- 22. We may denote the orange, yellow, light-green, dark-green, and blue groups by I, II, IV, and v, and the single lines of them by the arabic numbers, the place they occupy in each group being reckoned from the less to the more refracted. Thus by adding the chemical symbol of the gas we get a general method of denomination,

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according to which N II 5, N IV 6, N IV 7, and N V 2, for instance, indicate the brightest lines of the groups of the nitrogen-spectrum.

- 23. Not only is the general character of the two kinds of spectra we obtained when nitrogen was heated in our tubes, either by the direct discharge or by the discharge of the interposed Leyden jar, quite different, but the difference is even so great that the bright lines of one of the spectra do not in the least fall within the brighter part of the bands constituting the other. Thus, for instance, the bright yellow line (N II 5) falls within the nineteenth band, the darkest of all the bands constituting the less refracted part of the spectrum; the bright blue line (N V 2) falls into the darker part of one of the channeled spaces. Accordingly it appears by no means probable that by increasing the temperature the shaded bands of one spectrum may be transformed gradually into the bright lines of the other; nevertheless it would be desirable to prove by experiment that the passage from one spectrum to another is a discontinuous and abrupt one.
- 24. For a given nitrogen-tube which without the Leyden jar gives the spectrum of bands, and by means of the commonly used jar the spectrum of bright lines, you may easily select a jar of smaller covering, which, if intercalated, exhibits the curious phenomenon of two rival spectra disputing existence with each other. Sometimes one of the spectra, sometimes the other appears; and for moments both are seen simultaneously. Especially the brighter lines of the second spectrum abruptly appear in the blue and violet channeled spaces of the first, and, according to the fluctuation of the induced current, either suddenly disappear again or subsist for some time, and constitute with the added fainter lines the second spectrum.

We obtain in an easier and a continuous way both spectra simultaneously by making use of a small Leyden jar, and increasing its charge by an intercalated stratum of air the thickness of which increases till the bright lines appear within the bands of the primitive spectrum.

- 25. By these and other experiments it is evidently proved that ignited nitrogen shows two quite distinct spectra. Each bright line of one of these spectra, each of the most subtle lines into which, by means of the telescope, the bands of the other are resolved, finally depends upon the molecular condition of the ignited gas, and the corresponding modification of the vibrating ether within it. Certainly, in the present state of science, we have not the least indication of the connexion of the molecular constitution of the gas with the kind of light emitted by it; but we may assert with confidence that, if one spectrum of a given gas be replaced by quite a different one, there must be an analogous change of the constitution of the ether, indicating a new arrangement of the gaseous molecules. Consequently we must admit either a chemical decomposition or an allotropic state of the gas. Conclusions derived from the whole series of our researches led us finally to reject the first alternative and to adopt the other.
- 26. The same spectral tube exhibits, in any succession whatever, as often as you like, each of the two spectra. You may show it in the most striking way by effecting the intercalation of the Leyden jar by means of a copper wire immersed in mercury. As

often as the wire is taken out of the mercury we shall have the spectrum of bands; as soon as the communication is restored, the spectrum of bright lines. Hence we conclude that the change of the molecular condition of nitrogen which takes place if the gas be heated beyond a certain temperature by a stronger current, does not permanently alter its chemical and physical properties, but that the gas, if cooled below the same limit of temperature, returns again to its former condition.

27. The essentially different character of the two extremities of the first spectrum of nitrogen, as described (16–19), and the indistinctness of its middle part, suggested to us the idea that, in reality, the observed spectrum might originate from the superposition of two single spectra. Accordingly one of these single spectra, the more refracted part of which is best developed, must be formed by channeled spaces; the other one, the less refracted part of which is best developed, must be a spectrum of shaded bands. In different cases, either the one or the other of the spectra may be predominant.

In order to confirm our conjecture it was necessary to get the two spectra separated.

28. The discharge of Ruhmkorff's coil through a spectral tube is changed the less by introducing the Leyden jar, the weaker is the resistance opposed to it by the tube. Accordingly the two different degrees of temperature to which the gas rises by the discharge when, the coil remaining the same, we either make use of the jar or not, may be regulated in such a way as to approach one another more and more. tension of the gas of about 10 millims. remain the same, the temperature produced by the discharge will be diminished by increasing the interior diameter of the capillary Thus we succeeded in constructing a tube which, when the part of the spectral tube. direct discharge was sent through it, became incandescent with the most brilliant goldcoloured light, which might easily be confounded with the light of highly ignited vapours of sodium; but with the intercalated jar, the light of the incandescent gas within the same tube had a fine bluish-violet colour. The yellow light, when analyzed by the prism, gave a beautiful spectrum of shaded bands, extending with decreasing intensity to the blue, the channeled spaces being scarcely perceptible. The bluish light, when examined, was resolved by the prism into channeled spaces extending towards the red, while the former bands almost entirely disappeared. We may transform each colour and its corresponding spectrum into the other ad libitum.

Hence it follows that there is another allotropy of nitrogen, which, like the former, is not a stable and permanent one, but depends only upon temperature. The modification in which nitrogen becomes yellow corresponds to the lower, the modification in which it becomes blue to the higher temperature.

29. When we send the direct discharge of Ruhmkorff's coil through one of Geissler's wider tubes enclosing very rarefied nitrogen or air (the oxygen of air becomes not visible here), we see the negative pole surrounded by blue light, the light at the positive pole being reddish yellow. In such of Geissler's tubes as are especially calculated to show how the light starting in all directions from the different points of the negative electrode is by the action of an electro-magnet concentrated along the magnetic curves

passing through these points, the blue light is most beautiful. It belongs generally to the nitrogen alone, which, on account of the greater resistance at the negative electrode opposed to the discharge, reaches a higher intensity of heat there than at the positive pole. When analyzed by the prism, the blue light gives the spectrum of channeled spaces, with traces only of the less refracted bands. The reddish-yellow light of the positive pole is more faint, and therefore not so easy to be submitted to spectral analysis.

- 30. When Ruhmkorff's large induction coil is discharged in common air between two points the distance of which does not exceed a few centimetres, we obtain, as is well known, a brilliant spark surrounded by an aureola, the colour of which is partly bluish violet, partly reddish yellow. In order to separate these colours more distinctly from each other, the aureola, moved by the slightest breath, may be extended into a large surface by blowing it sideways. But the separation may be best made when the discharge takes place between the two poles of an electro-magnet in the equatorial direc-While the straight spark is not acted upon by the electro-magnet to any sensible degree, the aureola is expanded into a fine surface, bounded by the spark starting from one to the other extremity of the electrodes, and by a semicircle passing through these At a certain rarefaction of air this surface appeared most beautifully bounded by a semicircular golden-coloured band, and divided by a similar band into two parts\*. We may explain now in a satisfactory way the appearance, hitherto mysterious, of the golden light. Both the yellow and the blue light are owing to the nitrogen of the air, reduced by the heat of the current into the two allotropic states which exhibit the spectra of channeled spaces and of bands. The brilliant white light of the spark partly belongs to the oxygen, partly to the nitrogen of the air, both highly ignited, the nitrogen being in that allotropic state in which it exhibits the spectrum of bright lines.
- 31. In order to complete the history of the spectrum of nitrogen we add two remarks. First, by intercalating a Leyden jar and, in order to weaken the current, at the same time a stratum of water or a wet thread, we may also reduce the spectrum of bright lines to the spectrum of bands. Secondly, by increasing the density of the gas, or, if the gas be less dense, by intercalating at the same time a large jar and a stratum of air, the bright lines of the spectrum, at the highest obtainable temperature, will expand. Out of a great number of observations made in this direction we shall describe only one.
- 32. A short spectral tube enclosing nitrogen of a tension of about 250 millims. refused passage to the discharge of Ruhmkorff's large induction coil, when three of Grove's elements were made use of and the jar intercalated. Without the jar the discharge passed through and produced a bright but rather undefined spectrum of bands. When the current continued to pass, the indistinctness of the spectrum increased, and after short intervals brilliant coloured lines appeared and disappeared again, like lightning-flashes. These lines, occupying always the same place, belonged to the second spectrum of nitrogen, the brightest yellow and green lines of which

<sup>\*</sup> Plücker, "Ueber die Einwirkung des Magnetes auf die elektrische Entladung," Poggendorff's 'Annalen,' vol. exiii, p. 267.

(N II 5, N IV 6, N IV 7) were specially observed. When we made use of twelve of GROVE'S elements ranged into three sets of four combined ones, the current even passed after we interposed the jar, and we got a most dazzling second spectrum of the gas. The bright lines of this spectrum, rising from a ground itself brighter than it usually is, ceased at an increased brilliancy to be well defined. The two brilliant green lines both expanded, and were united into a single broad line; the double yellow lines, though expanded, yet remained double. The spectrum was progressing towards a continuous one.

33. In recapitulating, we get the following results:—

Nitrogen in the state of greatest rarefaction, such as may be obtained by Geissler's exhauster, like other gases does not allow the induction current to pass through. when its tension is only a small fraction of a millimetre, the current begins to pass and renders the gas luminous. Below a certain limit of temperature ignited nitrogen sends out a golden-coloured light, giving the spectrum of bands. Above this limit the colour of the light is replaced by a bluish violet, the spectrum of channeled spaces replacing simultaneously the spectrum of bands. When, by means of the intercalated jar for instance, the temperature rises to a second higher limit, the light of the gas, becoming white and most brilliant, gives, if analyzed by the prism, a spectrum of quite a different description: bright lines of different intensity, with the colour indicated by the place they occupy, rise from a dark ground. By increasing the power of the discharge these lines become more brilliant, but the brilliancy does not increase in the same ratio for New bright lines appear, which formerly, on account of their extreme faintness, were not visible; but the number of such lines is not unlimited. By increasing the heat of the ignited nitrogen to the last extremity, the lines, especially the brighter ones, gradually expand, approaching thus to a continuous spectrum.

34. Those spectra which are composed of larger bands showing various appearances according to their being differently shaded by subtle dark lines, we generally call spectra of the first order. In the same spectrum the character of the bands is to a certain extent the same, the breadth of the bands varies in a more or less regular way. On the contrary, those spectra in which brilliant coloured lines rise from a more or less dark ground, we call spectra of the second order.

Ignited nitrogen therefore exhibits, if its temperature increase, successively two spectra of the first and one of the second order.

35. In the case of sulphur, which we may select as another instance, there are two different spectra, one of the first and one of the second order.

In common air the flame of sulphur gives a continuous spectrum; if fed with oxygen we get a spectrum of the first order, but it is faint and its bands are not well defined. In order to get the sulphur-spectrum most perfect, we must recur to our spectral tubes.

A doubly bent short tube (6), into which we introduced a small quantity of sulphur, was evacuated by means of Geissler's exhauster, and while attached to it heated by a lamp, in order to expel as much as possible the moisture it contained. Finally, the manometer showing no more tension of the remaining gas, the tube was hermetically sealed

by a blowpipe. The direct charge of Ruhmkorff's large induction coil sent through it, generally indicates by their spectra traces of remaining foreign substances (8). But when the tube was heated by a small alcohol-lamp, at a certain moment a fine sulphurspectrum of the first order appeared, undisturbed by any former spectrum. The beauty of the spectrum increased when we continued to heat moderately.

- 36. We counted thirty-seven well-defined bands, extending nearly from  $H\alpha$  to  $H\gamma$ . Seven of these bands, the first of which was of a dark-red colour and visible only under favourable circumstances, preceded the sodium-line, eighteen fell between this line and  $H\beta$ , and eleven between  $H\beta$  and  $H\gamma$ , the last of which being broader, appears sometimes divided into two. After a last band, traversed by  $H\gamma$ , a larger and strongly shaded space extended towards the extreme violet. The breadth of the bands increased from the less to the more refracted part of the spectrum. In each band, contrary to what takes place in the case of nitrogen, namely, with regard to its channeled spectrum, the shading produced by fine dark lines decreases from the less to the more refracted extremity. The darkest part of the shadow is bounded by a small separate band of a varied appearance, generally formed by two small bright lines including a somewhat larger dark one. By these small bands the purely channeled character of the spectrum is disturbed.
- 37. If, while the discharge is passing, we continue to heat the tube by a lamp, the brightness of the spectrum always increases; but if we approached to a certain degree of temperature, in different parts of the spectrum we have described, bright-coloured lines belonging to the sulphur-spectrum of the second order appeared and disappeared again according to the fluctuating heat, till at last the second of the two rival spectra remained undisturbed. The colour of the light was changed. In cooling again after the lamp was taken off, the light within the tube changed its colour again, while the spectrum of the second order was replaced by the spectrum of the first order.

There is a certain elevation of temperature at which the increased density of the vapour does not permit the discharge to pass; the light within the tube is extinguished, but abruptly reappears after cooling.

38. Well-defined bright lines, constituting a fine sulphur-spectrum of the second order, are obtained if moderate discharges of Rhumkorff's large induction coil are sent through the tube, the tube being slightly heated by means of an alcohol-lamp, and a small Leyden jar being intercalated. At first the spectrum extends only from about the sodium-line to  $H\beta$ . One observes chiefly a characteristic group of sixteen lines, followed at some distance by two separate lines. The spectrum once developed persists even after taking off the lamp. When we continue to heat, the brightness of the group increases and its lines begin to expand, while at the same time the hitherto black ground is coloured. The brilliancy may be increased to such an extent as to be unbearable to the eye. Beyond the sodium-line, towards the red extremity, new distinct lines appear, among which we particularly distinguish a triple line, remarkable as well for its fine red colour as for its distinctness, and nearer to  $H\alpha$  a second such triple line, at first well

defined but soon merging into a single one. Like the less refracted part of the spectrum, the most refracted part is developed only at a higher ignition of the vapour of the sulphur. At its violet extremity (we do not give here a full description of the middle part) we observe at the same distance from one another five well-defined fainter bright lines. Then follows, after an expanded violet band, a group of four bright lines, the second of which is accompanied by a more refracted, the fourth by a less refracted faint line. The fourth line especially is distinct to a degree seldom observed at so high a refraction and so great a power of the discharge. After two bands of faint light, there is seen at the end of the spectrum a group of four slightly expanded bright lines, preceded by an expanded violet band.

- 39. Like sulphur, selenium has two spectra—one of the first, another of the second order.
  - 40. Ignited carbon, even in a state of greatest division, gives a continuous spectrum.
- 41. We select, among the various compound gases which, if decomposed in flame, give the spectrum of carbon, in the first place *cyanogen*. The gas was procured by heating cyanide of mercury introduced into a retort of glass by means of a lamp. The flame of it may be fed either with oxygen or with air.

When a jet of cyanogen mixed with oxygen is kindled, in the interior part of the flame a most brilliant cone of a whitish-violet light is seen, the limit between the ignited and the cold part of the jet. This cone exhibiting the spectrum of vapour of carbon best developed, we conclude that the cyanogen must be decomposed into carbon and nitrogen, the carbon being in the gaseous condition a moment before its combination with oxygen takes place\*.

42. In order to prevent explosion of the mixture of cyanogen and oxygen, it is preferable that the jets of the two gases meet from opposite sides before the slit of the spectral apparatus, forming there, if kindled, a brilliant, flat, vertical surface. The jet of cyanogen might be obtained directly from the retort, by the heating of which it may be Thus we get, all being properly arranged, a splendid and richly coloured regulated. Especially we distinguish eight groups of bright lines, which, being all of the same general character, indicate at first sight the existence of vapour of carbon. We shall denote these groups, starting from the less refracted and proceeding to the more refracted ones, by a, b, c, d, e, f, g, h. The group a is formed by five, b by six, c by four, d by five, e by seven, f by three, g by seven, and h by three bright lines. But these lines, of a measurable breadth and a quite different appearance, are not to be confounded with the bright lines which, in the case of nitrogen and sulphur, for instance, constitute spectra of the second order. In each group the first line is the brightest; the following, which are nearer to one another, decrease in intensity, and under less favourable circumstances the last ones are not seen. Hence the groups, according to an expression of Mr. Attfield, have the appearance of a portico. The red group (a) is not always seen distinctly (less distinctly in the present case than in the case of other gaseous com-

<sup>\*</sup> Mr. Attributed has the merit of having first stated that spectra hitherto attributed to compound gaseous substances, are to be referred to the vapour of carbon itself (Philosophical Transactions for 1862, p. 221).

pounds of carbon); the group f is very faint, the group g beautifully violet, h rather ultra-violet.

43. The whole spectrum, except its red extremity, is divided into large shaded fields. The shadow increases from the less to the more refracted part of each field; from its orighter less refracted part arise the bright lines of one group, the first of these lines towards the darkest extremity of the preceding field. As well as in the former cases of nitrogen and sulphur, the shadow is produced by dark transversal lines on a coloured ground. But here the distance of the shading-lines from each other varies even in the same field. Towards the bright, i. e. the less refracted extremity of each field, the distance decreases, while at the same time the darkness and the breadth of the lines is diminished. The space between two consecutive lines appeared to be greatest in the field containing the group c, at a distance from d about twice as great as that from c. There we counted, on making use of two prisms and applying a magnifying-power of eighteen, the aperture of the slit being regulated in the ordinary way (13), nine shadinglines, including eight nearly equal small bands, the total breadth of which corresponded to five divisions of our arbitrary scale. Hence we computed the angular distance of two consecutive dark lines which we observed to be about five-fourths of the distance of the sodium-lines.

The dark shading-lines also appear within the bands bounded by the lines of the brighter characteristic groups. The band between the second and the third bright line of the yellow group b, the total breadth of which corresponds to four divisions of our arbitrary scale, was divided by dark lines into twelve smaller bands of about equal breadth. Accordingly the angular distance of two such consecutive lines is about two-thirds the distance of the two sodium-lines. The dark lines within the neighbouring band, bounded by the first and second bright line of the same group, were much nearer to one another, and their number too great to be counted with certainty.

- 44. Between the groups f and g there is indicated a particular distribution of light and shadow, which, being a faint copy of what takes place if olefiant gas be burned instead of cyanogen, will be better understood after we have described the spectrum of the new gas.
- 45. The least-refracted part of the spectrum, preceding the first line of the group a, essentially differs from the more refracted part already described. There are three fine red bands contiguous to the first bright line of the group, extending nearly to  $H\alpha$ , and beyond this hydrogen-line, after a dark space, two similar but not so well-defined bands. The breadth of these bands is nearly the same, and all are shaded in a similar way. Contrary to the distribution of shadow in the larger field, the shadow is strongest in the less refracted part of each band; in the most refracted part we observed two bright lines.
- 46. When the combustion of cyanogen took place in air, the bands we have just described were best developed, and new similar ones added. They extended from beyond  $H\alpha$  nearly to  $H\beta$ . The breadth of these bands slightly increases towards the violet end of the spectrum, their general description remaining the same. We especially counted seven such bands, the first of which is traversed by the double sodium-line, and the last

is bounded at the place formerly occupied by the second bright line of the characteristic group c.

When the flame of cyanogen is fed by air, we observe under favourable circumstances no traces of the groups a and b, the least-refracted bright line of the group c faintly appears, d is scarcely indicated, but the groups e, f, g are fully developed, especially the last one, of a fine violet colour.

46. In supplying the flame of cyanogen by air increasingly mixed with oxygen, we distinctly see two spectra overlying one another. One of these spectra (the spectrum of bands) giving way step by step to the other, the appearance is continually changed. The red bands only remained undisturbed, they became even more distinct by the increased intensity of the combustion. The adjacent group a is scarcely developed, evidently on account of an imperfect extinction of the overlying bands.

The superposition of the two spectra introduces new details into the general configuration of the resulting spectrum. Thus, for instance, at a certain intensity of combustion the interval between the first and second bright line of the group b is divided by four fine bright lines into five spaces, the breadth of which decreases towards the violet part of the spectrum. Thus also in the large field containing the group c, the influence of the spectrum of bands is rendered sensible by a particular distribution of shadow.

47. Secondly, we submitted to a closer examination olefiant gas, H<sup>4</sup>C<sup>4</sup>, when burned either with oxygen or with air. We operated as we did in the former case of cyanogen; only the gas, prepared by heating a mixture of alcohol and sulphuric acid, was previously introduced into a gasometer.

The luminous cone which exhibits the spectrum of vapour of carbon is of a fine blue colour, especially if the flame is fed by oxygen.

48. In the spectrum thus obtained the characteristic groups a, b, c, and d appeared on a shaded ground. All these groups, especially the red one  $\alpha$ , scarcely seen in the spectrum obtained by the combustion of cyanogen, are finely developed. The last line of b and d is slightly expanded; but there is no trace whatever either of the bands of the spectrum of cyanogen, if burned in common air, or even of the groups e and q. Instead of these groups there is quite a new configuration. Equally distant from the place which the groups occupied in the former spectrum, a small well-defined black band was seen, bounded on the more refracted side by a violet space, which, being of great brilliancy where it touches the band, was shaded gradually till the spectrum, not extending beyond the place of the group g, was extinguished. This violet space is traversed by well-defined dark lines, equally distant from each other, but more apart than the shading lines we described in former cases. The black band is bounded on its less refracted side by a bright line, having the breadth of the lines of the characteristic groups, which at a certain distance was preceded by a more diffused violet light, traversed, like the brilliant one on the opposite side, by dark but less distinct lines. Here also the faint group f appeared.

The distribution of light and shade producing the configuration just described is MDCCCLXV.

seen also, distinctly but faintly, in the spectrum we obtained by the combustion of cyanogen with oxygen, where at the same time the groups e and g are beautifully expressed (44).

49. Among the gases exhibiting the spectrum of vapour of carbon, when enclosed in our spectral tubes and decomposed by the heat of the discharge of Ruhmkorff's coil, we first select oxide of carbon. In operating with this gas as we did with nitrogen, we got, if the Leyden jar was intercalated, simultaneously the spectrum of vapour of carbon and the spectrum of oxygen; without the jar, the pure spectrum of vapour of carbon. In the last case the heat of the discharge is high enough to ignite vapour of carbon, but not sufficient to give the spectrum of oxygen. The single spectrum, as well as the combined one, is obtained accordingly ad libitum; whence we conclude that as the successive discharges pass through the spectral tube, the gas is alternately decomposed and recomposed again.

50. We shall in a few words describe the spectrum obtained without the jar, at a tension of the gas, when observed by means of the manometer before the spectral tube was sealed, of 32 millims.

Four characteristic groups only were seen, a, b, c, and d. When the current first passed, the band a appeared completely; after some time its two first lines only remained, rising as isolated bright lines from a dark ground; finally all the group disappeared. The groups b, c, and d remained nearly unchanged; there appeared only two bright lines of c, the place corresponding to the two following ones being very brilliant.

The whole spectrum was divided into large fields, similar to the fields we described in the case of the flame of cyanogen fed with oxygen. But in this case each field is bounded at its more refracted and shaded extremity by the first bright line of a characteristic group; the following lines, bordered by shading, rise from the lightest part of the adjacent field. In the new instance the fields are not bounded in the same way. After the group  $\alpha$  has disappeared, there is a differently shaded dark space, extending to the place of the third bright line of that group. In the remaining part of the spectrum we may distinguish seven shaded fields. The first goes a little beyond the first bright line of the group b, where it is bounded by a transversal line, dividing the band formed by the first two lines of the group into a dark less refracted and a light more Accordingly the first bright line rises from the dark end of the first field, the remaining lines from the light end of the second field. The second field does not reach the first bright line of the following group c, this line being nearly equally distant from the extremity of the field and the next line of the same group. The third field goes slightly beyond H $\beta$ ; the fourth to the first line of the group d; the fifth nearly to the place occupied by the fifth line of the group e; the sixth approaches the place of the group f; and the seventh extends to the fourth line of the group q. fourth and sixth fields presented the appearance of pure channeled spaces, as described in the case of nitrogén.

- 51. If the heating-power of the discharge be too strong, spectral tubes enclosing oxide of carbon at a higher tension showed only three large shaded fields, without any traces of the characteristic groups. The first two of these fields are coincident with the second and third of the former fields; the third occupies the place of the fourth and fifth former fields united into one. Here the shading of the three large fields not being disturbed by any additional appearance, the transversal shading lines were observed most distinctly even in making use of four prisms and employing a magnifying power of 36. In observing especially the light and less refracted part of the first field close to its extremity, these lines, on account of their extreme subtleness, are scarcely to be perceived; when they begin to become well defined they are very near to each other; but towards the more refracted part of the field their distance increases simultaneously with their breadth, till, at some distance from the bright extremity, the dark expanded lines are resolved into small shaded bands\*.
- 52. Spectral tubes containing *carbonic acid* instead of oxide of carbon gave essentially the same spectra. The increased quantity of oxygen of the decomposed gas may be observed by means of the interposed jar. In such tubes there was no carbon deposited, not even after a long passage of the discharge.
- 53. All compound gases enclosed in our spectral tubes are decomposed by the heat produced by the discharge of Ruhmkorff's large induction coil; but instantly after the discharge passes, the recomposition takes place. The recomposition is prevented only by a sudden cooling of the elementary gases obtained by the decomposition. Thus, for instance, spectral tubes enclosing cyanogen are scarcely fitted for observation, the interior surface of their capillary part being instantaneously blackened by the deposited carbon. No carburetted hydrogen resists final decomposition by the passing current. We add only a few observations, made by means of spectral tubes.
- 54. The spectrum of the light hydrocarbon gas,  $C^2$  H<sup>4</sup>, obtained without the Leyden jar, at once showed the expanded bright lines of hydrogen and an imperfect spectrum of vapour of carbon, especially the brightest lines of the characteristic groups b, c, and d. By intercalating the jar, the hydrogen-spectrum, approaching to a continuous one, became quite predominant.

Olefiant gas, C<sup>4</sup> H<sup>4</sup>, of a primitive tension of about 70 millims., gave, without the jar, a scarcely visible spectrum; by intercalating the jar, the three hydrogen-lines H $\alpha$ , H $\beta$ , H $\gamma$  appeared well defined, and the spectrum of vapour of carbon, with its groups a, b, c, d, and its shaded large fields, well developed.

Methyl, C<sup>2</sup> H<sup>3</sup>, showed, without the jar, at once H $\alpha$ , H $\beta$ , H $\gamma$ , and the characteristic groups e and g; with the interposed jar these two groups disappeared, and were replaced by the groups a, b, c, and d.

Acetylene, C4 H2, though according to Berthelot and Morren formed from its

<sup>\*</sup> The same spectrum, but fainter, is obtained under quite different conditions. We have already noticed, in the introductory remarks, that in a spectral tube evacuated to the last degree by Geissler's exhauster, vaporized carbon is indicated by its spectrum. The spectrum obtained is that described above (8).

elements when Davy's charcoal light is produced within an atmosphere of hydrogen, when introduced into our tubes is nevertheless rapidly decomposed by the discharge, and most incompletely recomposed after the discharge has passed. The inside of the tubes is instantly blackened, and in the first moment only, along with the spectrum of hydrogen, we perceive the groups of carbon-lines seen in the case of olefant gas.

55. Finally, Ruhmkorff's large induction coil was discharged between two electrodes of carbon, surrounded by an atmosphere of hydrogen. The four groups a, b, c, and d were obtained, constituting the spectrum of vaporized carbon.

56. In resuming, we are struck by the variety of appearances presented by ignited vapour of carbon when submitted to spectral analysis under different conditions. whatever may be this variety, it is impossible not to admit that all or nearly all of the various types of spectra we described are derived from the same source. We may distinguish four such types: 1st, the bands, especially seen when the flame of cyanogen is fed by air; 2ndly, the particular distribution of light and shadow near H\beta when the flame of olefiant gas is fed by oxygen; 3rdly, the large fields shaded by transversal dark lines; 4thly, the characteristic groups of bright lines, a, b, c, d, e, f, g, h, which are to be ranged into two different sets, a, b, c, d, and e, f, g, h. It is a curious fact that all these different types, either fully developed or indicated only, are represented in the flame of cyanogen, if fed with oxygen, while in all the other cases we examined there are represented either a single type or two types, or even three,—namely, 1, the third type alone; 2, the first type, with the second set of groups; 3, the third type, with one set of groups (a, b, c, d); 4, the same type, with the other set (e, g); 5, the second and third types, with the first set of groups. There is no doubt that the different types correspond to different degrees of temperature,—the temperature being lowest when the bands are principally developed, lower in the case of the second set of groups than in the case of the first, lower in the case of the shaded large fields than in the case where the characteristic groups appear simultaneously.

In the present state of the question we are not able fully to explain the various types of spectra of carbon. It is only proved that all spectra which we referred to carbonic vapour do not contain any bright line belonging to another elementary gas. Either the well-known spectra of foreign admixed gases, of nitrogen, oxygen, hydrogen, for instance, do not appear at all; or if they do, they may be subtracted from the whole apparent spectrum.

It appears doubtful that the different types depend solely upon temperature. If so, the temperature varying in the different parts of the ignited vapour of carbon, different types may be seen simultaneously. We shall not now discuss the influence which the coexistence of foreign gases might have on the spectra of vapour of carbon, nor may we here decide whether or not, in the lower temperature of the flame, a gaseous compound of carbon, not being entirely decomposed, exhibits, with the spectrum of the vapour of carbon, simultaneously the spectrum of the undecomposed gas.

In the spectrum of cyanogen, for instance, we got no visible traces of the spectrum

of nitrogen (originating from the decomposed gas), whether we supplied the flame by a jet of oxygen, or operated in open air; but in both cases there is no reason not to admit that the bands, which are not seen in the case of any other compound of carbon, were owing to the undecomposed cyanogen (see no. 61).

- 57. With regard to the spectrum of hydrogen, we first refer to former observations. The spectrum one of us obtained by sending the discharge of RUHMKORFF'S small induction coil through one of his highly evacuated spectral tubes, constructed by M. Geissler, shows only three bright lines, which he denoted by  $H\alpha$ ,  $H\beta$ , and  $H\gamma$ . The beautiful red light of the ignited rarefied gas, divided into these three bright lines, even after having passed through the four prisms of Steinheil's spectral apparatus, remains highly concentrated. At a magnifying power of 72, the three bright lines or small bands thus obtained are well defined. Their apparent breadth is equal to the breadth of the slit; consequently, on further narrowing the slit, they approach gradually to mathematical lines. Hence we conclude that, under the above-mentioned conditions, the length of wave of the light constituting each of the three hydrogen-lines is constant, and remains so if by widening the slit the lines are expanded into bands. In referring the middle lines of such bands to the middle line of the direct image of the slit, we obtain its angle of refraction. It was proposed to employ these middle lines instead of Fraunhofer's dark lines of the solar spectrum in determining the indices of refraction\*. This proceeding has since been proved to be very expedient †.
- 58. Hydrogen permits the electric discharge to pass at a lower tension than other gases do. When Ruhmkorff's small induction coil was discharged through a spectral tube enclosing hydrogen, which was gradually rarefied to the highest tenuity to be reached by means of Geissler's exhauster, finally the beautiful red colour of the ignited gas became fainter, and passed gradually into an undetermined violet. When analyzed by the prism,  $H\alpha$  disappeared, while  $H\beta$ , though fainter, remained well defined. Accordingly light of a greater length of wave was the first extinguished  $\updownarrow$ .
- 59. Hydrogen shows in the most striking way the expansion of its spectral lines, and their gradual transformation into a continuous spectrum. When the direct discharge of Ruhmkorff's large induction coil is sent even through the old spectrum tubes enclosing hydrogen, the formerly obtained spectrum is essentially altered. By increasing the power of the coil, the violet line  $H\gamma$  first expands; while it continues to expand, the expansion of the bluish-green line  $H\beta$  becomes visible. Let the aperture of the slit be regulated so that the double sodium-line will separate into two single lines nearly touching one another. Then, the angular breadth of  $H\beta$  becoming two or three minutes, the breadth of  $H\gamma$  is about double. The expansion takes place as well

<sup>\*</sup> Poggendorff's 'Annalen,' vol. cvii. p. 497.

<sup>†</sup> Landolt: "Ueber die Brechungsexponenten flüssiger homologer Verbindungen," Poggendorff's 'Annalen,' vol. exvii. p. 353.

<sup>‡</sup> Plücker: "Ueber recurrente Ströme und ihre Anwendung zur Darstellung von Gasspectren," Poggen-Dorff's 'Annalen,' vol. exvi. p. 51.

towards the less as towards the more refracted part of the spectrum. H $\alpha$  remains almost unchanged after H $\gamma$  has passed into an undetermined large violet band, and H $\beta$  extended its decreasing light on its two sides. On employing the Leyden jar, and giving to the gas in our new tubes a tension of about 60 millims., the spectrum is already transformed into a continuous one, with a red line at one of its extremities. At a tension of 360 millims, the continuous spectrum is highly increased in intensity, while the red line H $\alpha$ , expanded into a band, scarcely rises from it. If the electric spark passes through hydrogen at the ordinary tension, the ignited gas on its way always gives the spectrum of the three expanded lines\*.

60. Even in the old spectral tubes enclosing highly rarefied hydrogen, the ground, from which the three characteristic lines rise, did not appear always of the same darkness; in some instances new bright lines appeared, especially in the neighbourhood of the sodium-line. In resuming the subject, we pointed out the existence of a new hydrogen-spectrum, corresponding to a lower temperature, but having no resemblance at all to the spectra of the first order of nitrogen, sulphur, &c. In this spectrum, of a peculiar character, if fully developed, we observe a great number of well-defined bright lines, almost too numerous to count and represent by an engraving, but brilliant enough to be examined at a magnifying power of 72, after the light has passed through four prisms.

\* After Fraunhofer, and especially Dr. Wheatstone, directed the attention of philosophers to the electric spectrum, Masson indicated the red hydrogen-line, but without referring in an explicit way to its origin. Ansström first separated the spectrum of gas from the spectra of metal. In the diagram he gave of the hydrogen-spectrum, he represented, by means of curves, the intensity of light along the whole length of the spectrum, especially the maxima of intensity within the red, the green, and the violet. These maxima correspond to  $H\alpha$ ,  $H\beta$ ,  $H\gamma$ , here expanded into bands, the breadth of which, as well as their decreasing intensity towards both ends, are indicated by the extension and steepness of the curves. After one of us published his first researches on the spectra of ignited gases, M. van der Willigen, in operating with strong induced currents, determined in a similar way the maxima of intensity of the hydrogen-spectrum.

The spectra thus obtained are not calculated to prove the connexion existing between the bright lines of ignited gases or vapours and Fraunhofer's dark lines of the solar spectrum. Starting, in his first communication made to the Royal Swedish Academy, 1853, from the theoretical conception "that the dark lines of the solar spectrum are to be regarded as an inversion of the bright lines of the electric spectrum," M. Angström concluded the coincidence of Ha with Fraunhofer's line C; but the diagram shows that this conclusion was not based on exact measurement. One of us, in his publication of 1859, not being guided by any theoretical view on this point, first announced the coincidence of H $\beta$  with Fraunhofer's F, and fixed the position of H $\gamma$ near G, of Hα at a distance of two minutes from C. When at a later period he made use of Steinheil's large spectral apparatus, he pointed out at first sight the exact coincidence of  $H\alpha$  with C,  $H\gamma$  with a marked black line at some distance from G, towards F. In operating with spectral tubes, M. Angström confirmed these results. (The spectroscope employed in 1859 being a small and imperfect one, there was given to the slit an aperture of more than three minutes. The adjustment was made with regard to  $H\beta$ . Hence the error finally made in determining the position of Ha may be fully explained, by the circumstance that the illuminated border of the slit was observed instead of the illuminated aperture itself.)—Angström: "Optische Untersuchungen," Poggendorff's 'Annalen,' vol. xciv.; "Ueber die Fraunhoffer'schen Linien im Sonnenspectrum," Ibid. vol. exvii. Van der Willigen: "Over het electrische Spectrum, Verhandelingen der K. Hollandsche Academie (Natuurkunde vii. & viii.). Plücker, Poggendorff's 'Annalen,' vol. evii. p. 544.

61. On sending the direct discharge of Ruhmkorff's coil through a tube of glass from one-fourth to one-eighth of an inch in diameter, provided with electrodes of platinum or of aluminium, enclosing hydrogen at a tension of 5 to 10 millims., a luminous thread of light of a bluish-white colour was seen passing along the axis of the tube, without touching the glass. When analyzed by the prism, it gave a faint spectrum of the above-mentioned numerous bright lines, especially within the red and the yellow. Among these lines neither  $H\alpha$  nor  $H\gamma$  were seen;  $H\beta$  only appeared, but less bright than many of the other lines. By interposing the Leyden jar and gradually increasing its charge (12), all lines became brighter,  $H\beta$  surpassing all other lines in brilliancy;  $H\alpha$  appeared beautifully,  $H\gamma$  fainter. Hence we conclude that the numerous bright lines belong neither to the vaporized metal of the electrodes, nor to the decomposed interior surface of the glass, but solely to the hydrogen, constituting a new spectrum of it. This spectrum may be seen simultaneously with the three characteristic lines  $H\alpha$ ,  $H\beta$ ,  $H\gamma$ ; but at an increased temperature, when these lines begin to expand, it entirely disappears.

62. We got only one spectrum of oxygen in operating exactly in the same way as we did in the case of nitrogen, with merely this difference, that under the same conditions a spectrum of equal brightness was obtained only by means of a stronger discharge. Accordingly if oxygen, enclosed in the spectral tube, be replaced by common air, the spectrum of the oxygen it contains does not appear until after interposing the Leyden jar.

We do not enter here into the detail of the oxygen-spectrum, but conclude with a general remark. Nearly all luminous lines of the spectra of the second order expand when the temperature of the ignited gas increases beyond a certain limit; but neither do all lines reach the same brightness before expanding, nor do the lines in the different parts of the spectrum expand at the same temperature. That is seen best in the spectrum of the second order of oxygen. The bright lines constituting the characteristic groups of its middle part oppose the greatest resistance to expansion. If they are best defined, the luminous lines towards the red extremity, most distinct at a lower temperature, are already expanded, while towards the violet extremity the luminous lines are scarcely developed; they will be brightly developed, become well defined, and extend very far, after the ignited oxygen reaches a temperature at which the groups of the middle part are expanded. Hence arises the difficulty of representing the oxygen-spectrum. A drawing exhibiting the well-defined lines successively developed in its different parts is rather an ideal image than a true representation of nature.

63. Water introduced into a small spectral tube was kept boiling till the last traces of air were expelled, and then, before all the water was evaporated, the tube was hermetically sealed. The direct discharge, if passing, scarcely rendered the tube luminous, but with the intercalated jar the peculiar red light of hydrogen appeared, exhibiting the characistic lines  $H\alpha$ ,  $H\beta$ ,  $H\gamma$  well defined. When these lines became gradually expanded, the lines of the oxygen-spectrum successively appeared with an increasing intensity,

finally rising from the hydrogen-spectrum transformed into a continuous one. Here the heat of the discharge is increased by the increased density of the vapour of water, and reciprocally the evaporation is accelerated by the rising temperature of the discharge. The vapour of water is decomposed by the discharge; the ignited hydrogen resulting from the decomposition exhibits a spectrum at a lower temperature than the resulting oxygen does. After the discharge ceases, oxygen and hydrogen are recomposed again to water.

64. Phosphorus, when treated like sulphur (35), exhibits a beautiful spectrum of the second order. Whatever may be the gradual change of the intensity of light produced by regulating as well the discharge as (by means of a lamp) the heat of the spectral tube, we get only one spectrum of bright lines successively developed. Among them there is one announcing at first sight the presence of vapour of phosphorus, a triple orange line, formed by two single lines of first intensity, and a third less bright one bisecting the interval between them. The other brightest lines are seen within the green.

We get no difference at all by introducing into the spectral tube either common or red phosphorus. After the current had passed for some time, common phosphorus was seen, within the tube, transformed into a subtle powder of the red kind.

65. Chlorine, Bromine, and Iodine were among the substances first submitted to spectral analysis by one of us. On resuming the subject we fully confirmed the formerly obtained results, that not any two of the numerous spectral lines, characterizing the three substances, were coincident.

By means of the electric current we got in all instances only spectra of the second order. We were especially desirous of ascertaining whether there existed a spectrum of iodine, corresponding to a lower temperature, the inverse or negative image of which agreed with the spectrum produced by absorption on sending sunlight (which, in order to prevent the influence of Fraunhofer's dark lines, may be replaced by the light of phosphorus in combustion) through a stratum of heated vapour of iodine. Thus, indeed, we obtain more than fifty shaded bands, the breadth of which decreases from the violet to the red, constituting a spectrum of the first order. The flame of hydrogen in open air was not fitted to ignite vapour of iodine introduced into it sufficiently. But by feeding the flame by oxygen we got a new spectrum. Large fields, shaded by dark transversal lines, differently bounded, but quite similar to the third type of the spectra of vapour of carbon, constituted a spectrum of the first order. But the spectrum we might have expected according to theory was not seen.

- 66. Arsenic, when treated like sulphur and phosphorus, gives a well-defined spectrum of the second order.
- 67. So does *mercury* when introduced into a spectral tube from which air is expelled, either by means of GEISSLER'S exhauster, or by boiling the mercury within it. After a slight heating of the tube by means of an alcohol-lamp the discharge passes; and having once passed, it continues to do so, even without the lamp. Vapour of mercury

opposing a comparatively small resistance to the passing current, we found it useful to intercalate at the same time a Leyden jar and a stratum of air. Thus, indeed, by regulating as well the density of the vapour as the thickness of the stratum, we obtained the best-developed spectrum.

The least quantity of mercury, if vaporized, becomes visible by the passing current. Especially when mixed with other metals like arsenic, antimony, &c., we may detect even the least traces of it, which would entirely elude chemical analysis. instance, we observed that arsenic, whatever may be its origin, is not free from mercury. After introducing a small quantity of it, which we heated by an alcohol-lamp when we placed it before the slit of the spectral apparatus, in a few moments four lines of great brightness, among which was a double yellow one, rose from a dark ground, but before the spectrum was fully developed it was abruptly replaced by another quite as brilliant. The first spectrum obtained belongs to vapour of mercury, first developed by evaporization, the second to arsenic, which increasingly vaporized at a higher temperature disputes the conduction of the discharge with the mercury, the vapour of which, according to its small existing quantity, reaches only a very low limit. The spectrum of arsenic remaining alone, gradually increased in brilliancy by the development and expansion of its bright lines. In cooling the spectral tube, by taking off the lamp, the spectrum of arsenic lost its extreme brilliancy; well-defined bright lines, the number of which gradually diminished, rose from a dark ground, and were replaced again by the spectral lines of mercury, till finally all light was extinguished.

- 68. The metals of alkalies, sodium, potassium, lithium, thallium show, even at the lower temperature of Bunsen's lamp, a spectrum of the second order, consisting of bright lines, the number of which is increased by the higher temperature of the current, while the principal ones are expanded.
- 69. Barium, strontium, calcium show, even in Bunsen's lamp, shaded bands, and a bright chief single line at the same time. This line, green in the case of barium, bluish violet in the case of strontium, violet in the case of calcium, fully exhibits the character of the bright lines in the spectra of the second order. The bands, if well developed, constitute a spectrum of the first order. We examined especially the spectrum of barium, by introducing its chloride into the hydrogen-flame. In making use of two prisms and employing a magnifying power of eighteen, we distinctly obtained the shading of the bands resolved into dark lines, finer and closer to one another than in former similar cases. Thus we proved that the band-spectrum of baryta is in every respect a spectrum of the first order.
- 70. Spectra of the first order were observed in the case of a few heavy metals only. Among these metals we mention in the first instance lead. We obtain its spectrum in Bunsen's lamp, but in order to get it beautifully developed we must make use of the oxyhydrogen flame. The spectra we obtained were identically the same whatever compound of lead was introduced into that flame. We especially examined its combinations with chlorine, bromine, iodine, and oxygen. In all cases we observed larger bands,

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which by increased temperature were divided into smaller ones. Each band has a channeled appearance produced by fine dark lines, the darkness of which increases from the more to the less refracted extremity of the band, contrary to what takes place in the violet channeled spaces of nitrogen.

Chloride of lead, when examined within our spectral tubes, showed no traces of bands; they were replaced by bright lines. But on account of the great difficulty of vaporizing it, the spectrum of the second order, owing to lead, is best developed by the discharge of Ruhmkorff's coil between two electrodes made from this metal and surrounded by an atmosphere of hydrogen. The spectrum of this gas being under these conditions nearly a continuous one (59), the bright lines of the lead-spectrum of the second order rise from a coloured ground. More than fifty lines were counted, although the fainter ones did not appear.

- 71. When either chloride or bromide or iodide of copper is introduced into the flame of Bunsen's lamp, we get spectra of bands, but these bands are not exactly the same, they differ from one another by additional bands\*. In the oxyhydrogen flame the bands are better developed, but we did not succeed in resolving the shadows of the bands into dark lines. At the same time four lines of single refrangibility appeared. The number of these lines was increased and the number of bands reduced, when chloride of copper was examined within our spectral tubes. The well-known spectrum of the second order was fully developed, and every trace of bands extinguished, by discharging Ruhmkorff's coil between two copper electrodes.
- 72. Finally, manganese exhibited a curious spectrum of the first order, most similar to that of carbon (third and fourth type (56)). The whole spectrum is equally divided into large fields, but these fields are shaded differently by fine transversal lines, the shadow increasing from the more to the less refracted extremity of each field. From the brighter less refracted part rise groups of bright lines, similar to the groups of carbon, but the lines of the groups are differently distributed.

When Ruhmkorff's large coil was discharged between two electrodes made from manganese (we surrounded them with an atmosphere of hydrogen), a pure spectrum of the second order, free from any traces whatever of the former spectrum, was obtained.

#### EXPLANATION OF THE PLATES.

In determining the different spectra both of the first and the second order, the dispersing prisms occupied invariably the same position, corresponding to the minimum deviation of the green hydrogen-line H $\beta$ , *i. e.* of Fraunhofer's F. All spectra represented in the Plates are referred to the three hydrogen-lines H $\alpha$ , H $\beta$ , H $\gamma$ , and the double sodium-line Na. Generally two prisms of about 60° and 45° were employed,

\* This fact has been noticed by M.A. MITSCHERLICE with regard to the chloride and the iodide, and attributed by him to the undecomposed salt (Poggendorff's 'Annalen,' 1862, vol. ii. p. 299).

giving the distances of  $H\alpha$  and Na on one side and of  $H\gamma$  on the other side from  $H\beta$ , by the following numbers of divisions of an arbitrary scale:

139.6, 100.5-101, 88.5.

In the first Plate portions of all the coloured spectra are represented as they appear by making use of two additional prisms of 45°.

#### PLATE I.

contains spectra of the first order. The first spectrum, N, belonging to nitrogen, is taken under such conditions that both its extremities appear equally developed. To the whole spectrum is added a representation of two bands, C, of its more refracted part, obtained by means of the four prisms. Here a determined number of subtle dark transverse lines produce the channeled appearance. Likewise the configuration of two orange bands, A, and two green ones, B, is represented, exhibiting the character of the less refracted part of the spectrum (15–19, 27, 28).

S represents the spectrum of sulphur, as obtained by means of an exhausted bent spectral tube enclosing sulphur moderately heated by an alcohol lamp, and traversed by the charge without an interposed jar (35, 36).

Two green and two blue shaded bands, as seen by means of the four prisms, are represented by A and B.

C<sub>I</sub> shows the spectrum of vapour of carbon obtained by the combustion of cyanogen in oxygen. It exhibits within the large shaded fields groups of peculiar bright lines, the brilliancy of which it was impossible to represent. These groups are denoted by a, b, c, d, e, f, g, h. The red extremity becomes fainter when the heat of combustion increases, and even appears more distinct if the combustion takes place in air (41-46).

The configuration of one of the red bands, as seen when the four prisms are employed, is represented by A.

CII exhibits the spectrum of vapour of carbon obtained by means of spectral tubes enclosing oxide of carbon, the gas being decomposed by the electric discharge (49, 50). On taking away all characteristic groups, the remaining part of the spectrum, consisting only of three large shaded fields, is that obtained if the density of the gas be greater and the discharge too strong (51), as well as in the case of imperceptible traces of decomposed carbonic combinations (8).

CIII shows the less refracted part of the brightest of the large shaded fields (51).

C IV exhibits a peculiar distribution of light and shade within the violet, scarcely indicated in C I, but well developed when olefiant gas instead of cyanogen is burnt in oxygen (48).

### PLATES II. & III.

represent spectra of the second order, on a scale one-third larger than the scale of Plate I.

In Plate II. N shows the second spectrum of nitrogen (20-23), O the spectrum of oxygen (63), S the second spectrum of sulphur (37, 38), Se of selenium (39).

In Plate III. I shows the spectrum of iodine, Br of bromine, Cl of chlorine. Some remarks may be added here with regard to the conditions under which the spectra are obtained.

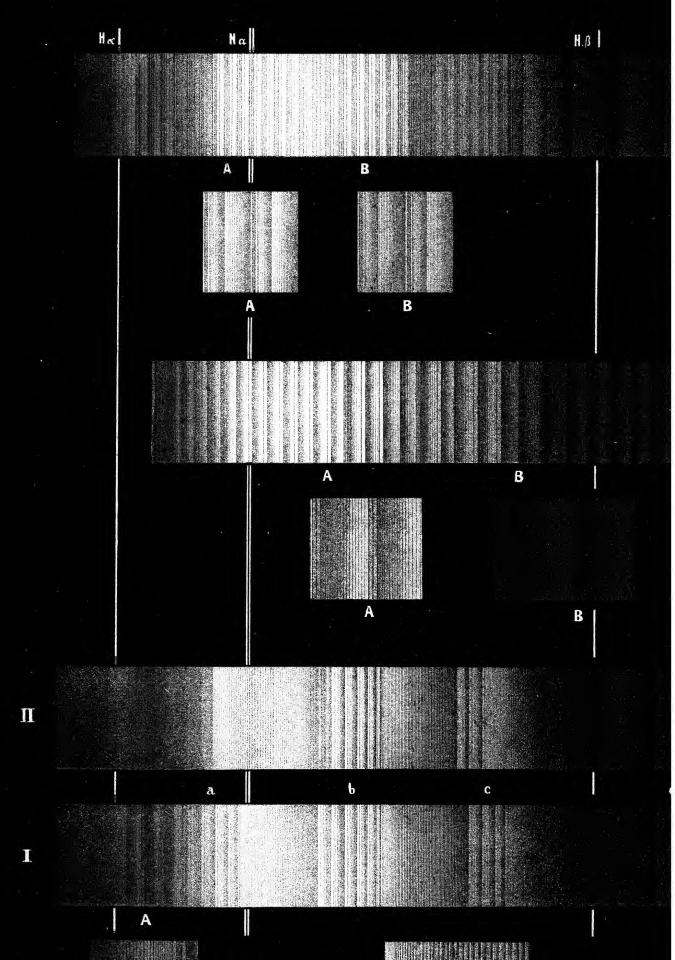
Iodine was introduced into a bent spectral tube, and the tube exhausted as far as While more recently tubes have been constructed which do not allow the discharge of RUHMKORFF's large coil to pass, not even at a very short distance of the electrodes, the same effect will scarcely be obtained if iodine is enclosed in the tube. Accordingly the very first moment the phenomena described in art. 8 take place; but soon after, vapour of iodine is developed, and by the heating power of the discharge we get, without the Leyden jar, a spectrum of mere iodine, consisting of very well-defined lines on a dark ground. After the interposition of the jar these lines became more brilliant, but remained well defined, and their number increased. Then the position and the intensity of the lines of the middle part were determined, while the red extremity was not at all developed, and the violet one most imperfectly. If the density of the vapour is increased by heating the tube by means of an alcohol lamp, the lines deter-The brilliancy so increases mined are expanded, while the ground becomes illuminated. that the eye can scarcely bear it, till at last the discharge ceases to pass. middle part approaches to continuity, a certain number of delicate brilliant red lines, seen in the diagram, appear, and do not lose their distinctness as long as the discharge Towards the violet extremity new lines likewise appear, but though that extremity becomes most brilliant, we were not able to get the lines well defined. the position of the expanded lines is approximately indicated by dotted lines.

A drop of bromine was introduced into a small exhausted spectral tube. The tension of its vapour being too great to allow the discharge to pass, the vaporized fluid was expelled till the remaining vapour obtained a tension of about 6 centimetres. But by and by the vapour of bromine, combined with the platinum of the electrodes, was deposited on the interior surface of the tube, and after some time, evidently from want of sufficient conducting matter, the beautiful spectrum fainted almost suddenly. The spectrum was taken with the interposed jar. In this case  $H\alpha$  and  $H\beta$  are simultaneously seen, but expanded, indicating traces of remaining water. The lines of oxygen are not seen. Without the jar hydrogen is not indicated. Then four bright lines, belonging to bromine, appear in the neighbourhood of  $H\alpha$ . While, with the interposed jar, they are fully expanded like this hydrogen-line, a less refracted subtle line appears, always remaining most distinct. The blue and violet extremity of the spectrum is better defined than in the case of iodine.

The spectrum of chlorine is taken under similar conditions with the spectrum of bromine. The spectral tube most carefully exhausted was several times filled with chlorine and exhausted again. The final tension of the remaining gas was about 6 centimetres, as it was in the former case.

P exhibits the spectrum of phosphorus (64).

We conclude with a general remark regarding more or less all the spectra of the second order represented in Plates I. & II. The intensity attributed to the different bright lines constituting these spectra corresponds to the condition in which they are best developed. There seems to be a general rule that all luminous lines become brighter and are finally expanded, when the heating-power of the discharge continually increases. But for different lines the intensity does not rise in the same ratio: thus lines less brilliant at first than others may afterwards surpass them in brilliancy. The intensity attained by the different luminous lines before they are expanded greatly differs; lines may disappear by expansion, while others of the same spectrum do not yet appear. The least-refracted lines generally resist expansion the most.



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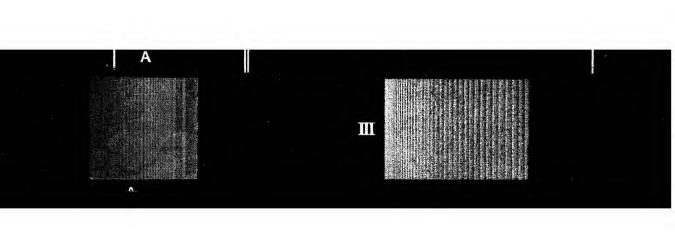
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Trans. MDCCCLX V. Plate 1.

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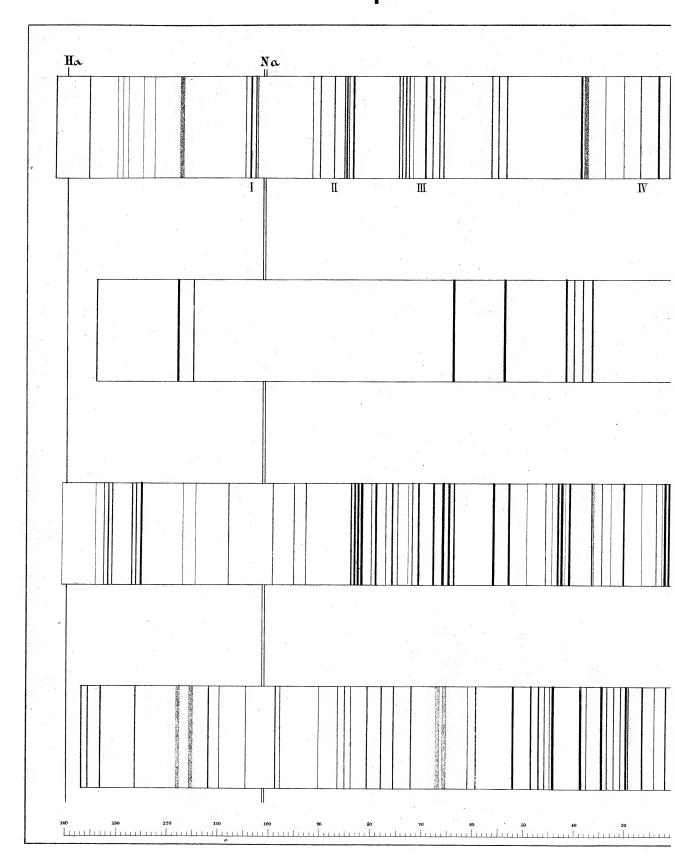


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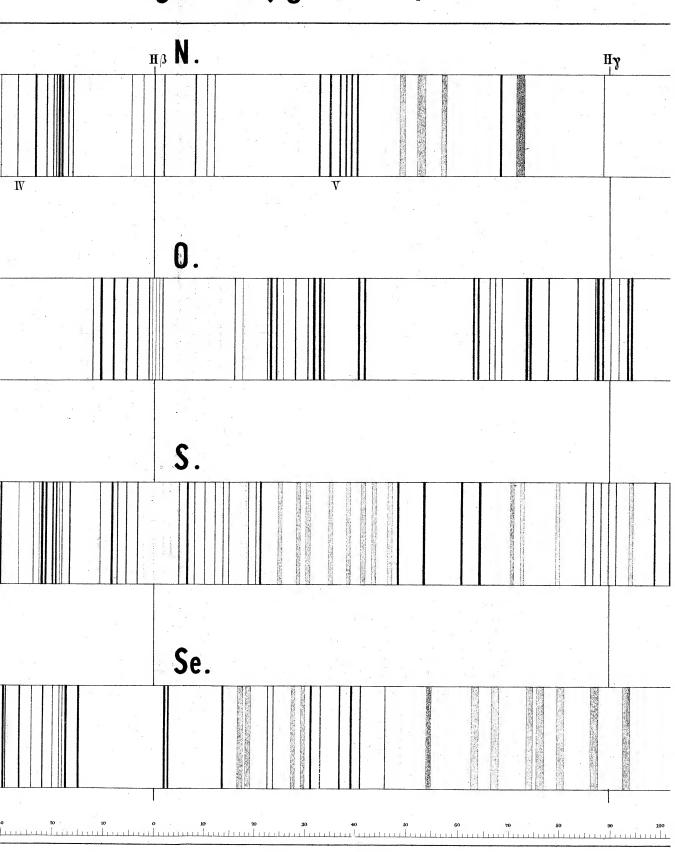
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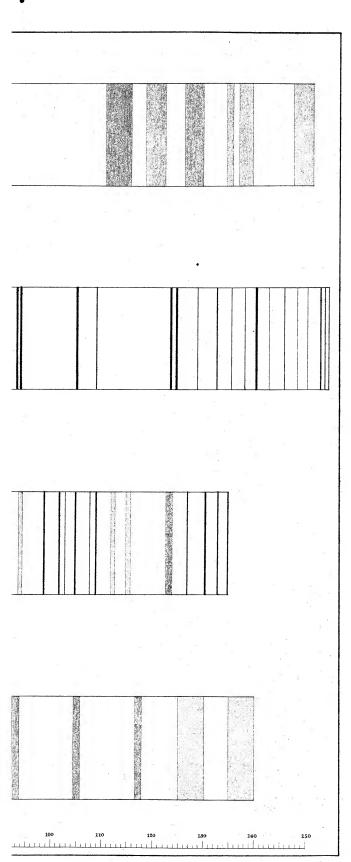
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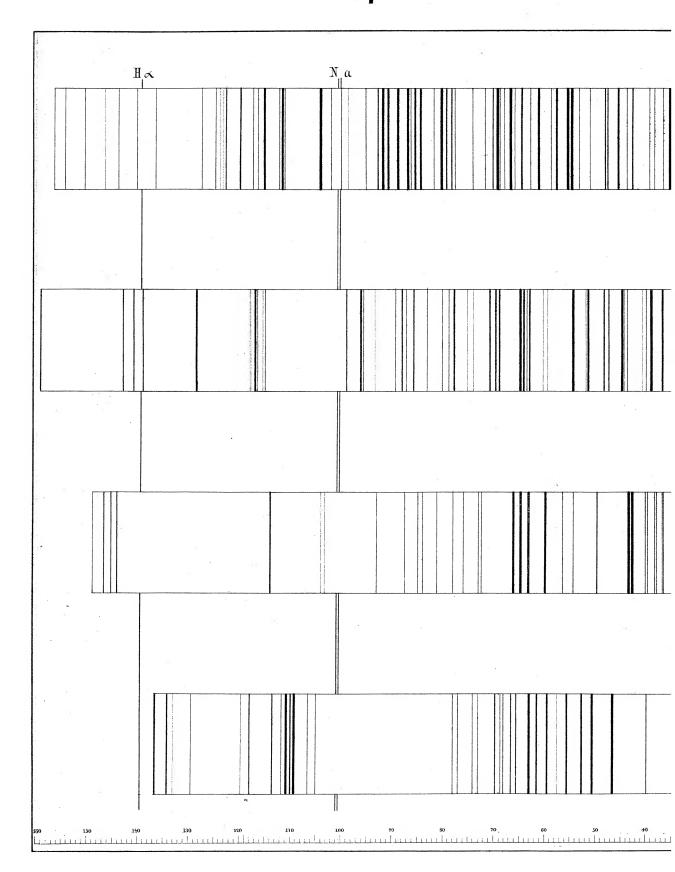
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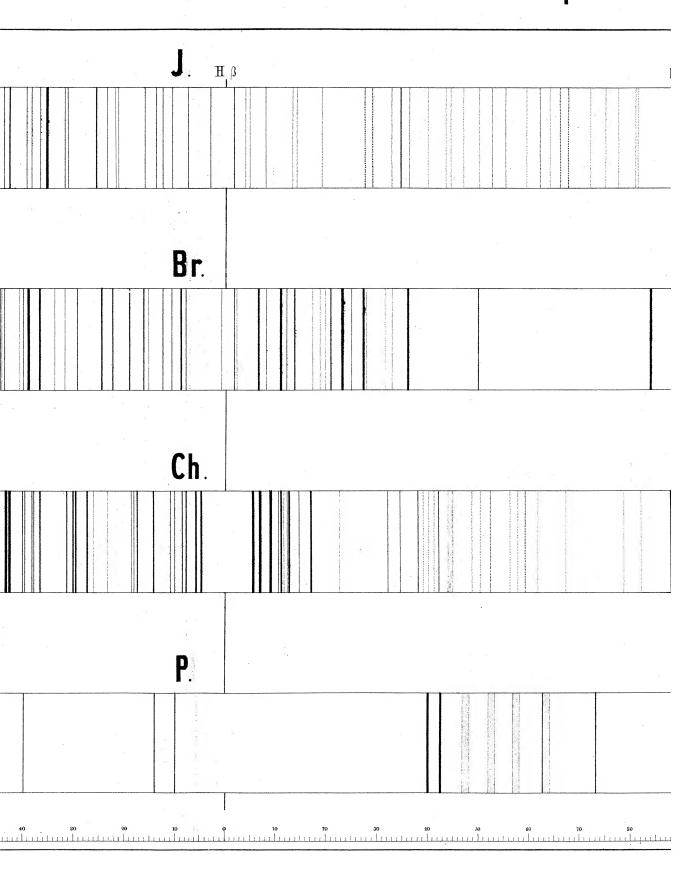


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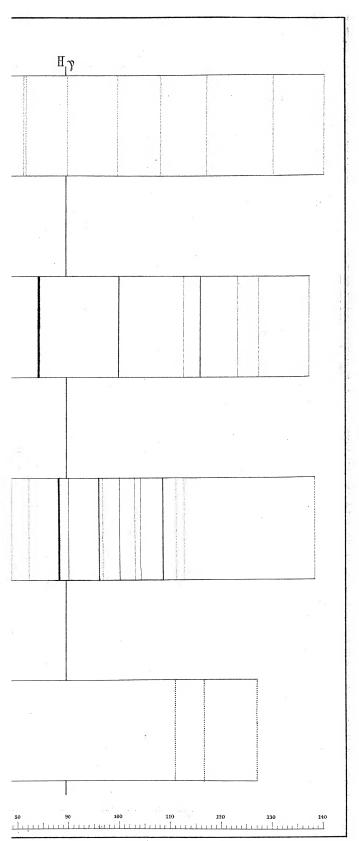
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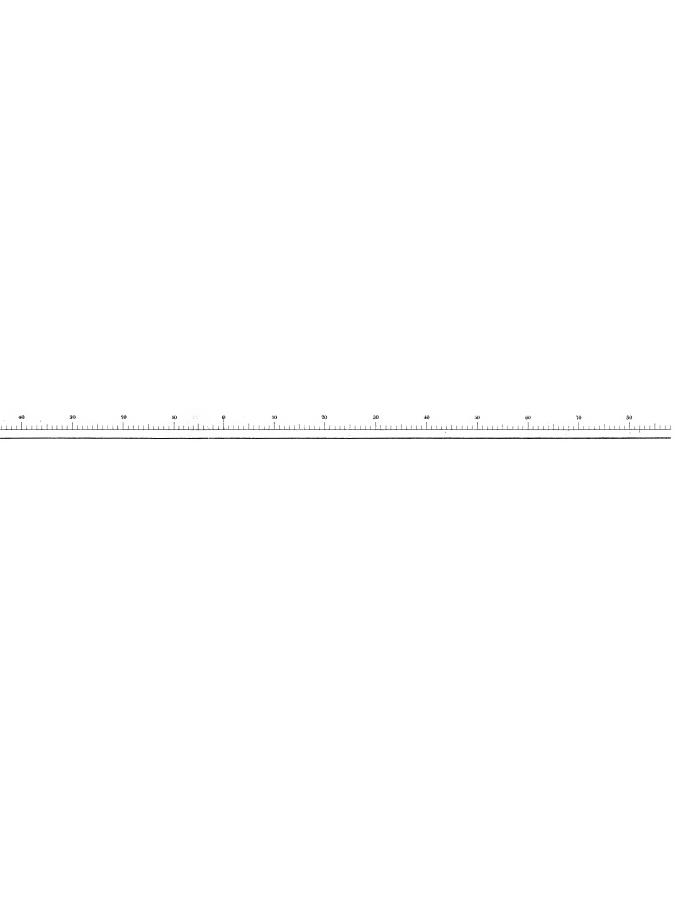


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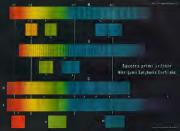
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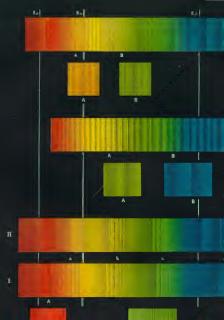
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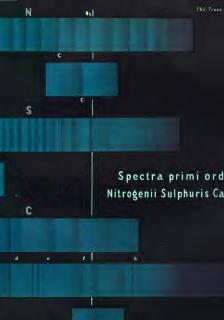


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